PRESSURE DEPENDENCE OF ELECTRIC SUSCEPTIBILITY OF CIS-1, 2-DICHLOROETHYLENE AT 9231 MH_z

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ABSTRACT. Pressure variation of the electric susceptibility of cis-1, 2-dichloroethylene in the vapour phase has been studied at a frequency of 9231 MH_z. It is found that the susceptibility varies linearly with pressure. Its value as computed from Van Vleck and Weisskopfs' expression at a known pressure after neglecting the effect of (P_E+P_A) is found to be equal to the observed value. It is therefore concluded that the contribution of atomic and electronic polarisations is negligible.

INTRODUCTION

The dielectric properties of a medium can be represented by a complex dielectric constant $\epsilon = \epsilon' - j\epsilon''$, where the imaginary part is the dielectric loss factor. The real part ϵ' is the dielectric constant and the quantity $(\epsilon' - 1)$ is known as electric susceptibility. The total electric susceptibility of a substance depends upon the various kinds of polarisations in the molecule. The main contribution is due to the dipole moment of the molecule. Since the dipole moment of this molecule is known, an attempt has been made to determine the contribution of atomic and electronic polarisations.

EXPERIMENTAL

A microwave video spectrograph has been used for the experiment. The experimental set-up consists of a klystron power supply, a 2K25 klystron, a frequency meter, attenuators, tuners, a standing wave detector, a six feet long waveguide cell, a vacuum system which can create low pressure of the order of 1μ H_g, a sensitive detecting device and a pressure gauge.

Hershberger's (1946) method has been used for the measurement of susceptibility. One end of the waveguide cell is fitted with a reflector thus producing standing waves in the system. The cell is completely evacuated and the position of minimum just outside the cell is located with the help of the standing wave detector. The vapour of cis-1, 2-dichloroethylene is then introduced into the cell and the shift in the position of minimum is noted carefully. The susceptibility is calculated with the help of expression

$$\delta = \frac{2\Delta L}{L} \times \left[1 - \left(\frac{\lambda}{2a}\right)^2\right] \qquad (1)$$

where ΔL is the shift in the position of minimum, L is the length of the waveguide cell, λ is the free space wavelength of microwave and a is the larger dimension of the waveguide cross-section. The experiment is then repeated for different pressures of the substance upto a pressure of 21 cm Hg which is the maximum attainable pressure for this substance at the room temperature i.e., 34°C.

RESULTS AND DISCUSSION

Figure 1 shows the variation of measured value of δ with pressure. It is found that the electric susceptibility varies linearly with pressure.

The complete quantum mechanical expression for susceptibility has been derived by Birnbaum (1953) from Van Vleck and Weisskopfs' (1945) theory and has been obtained in a simplified form by Krishnaji and Srivastava (1958). The expression is :

$$= \epsilon' - 1 = \frac{3p(P_E + P_A)}{RT} + \frac{4\pi N}{3kT}\left[\mu^2 + 2\sum_v \sum_T f_v f_{J_T} |\mu_{ij}|^2 \left(\frac{\nu}{\nu_{ij}}\right)_2\right]$$

$$+ \frac{4\pi N}{3kT} \sum_v \sum_T f_v f_{J_T} |\mu_{ij}|^2 \left[F(\nu, \nu_{ij}) - 2\right] \qquad (2)$$

where the first term is the contribution of the atomic and electronic polarisations, second term is due to transitions away from the region of observation and the last term is due to transitions in the region of measurement. f_v is the fraction of the molecules in the vibrational states concerned and f_{J_T} is the fraction of the molecules in the lower rotational state and for an asymetric molecule it is given by

$$f_{J_T} = \frac{(2J+1)\exp(-\quad)}{\left\{\frac{\pi}{ABC}\left(\frac{kT}{h}\right)^3\right\}^{\frac{1}{2}}} \qquad (3)$$

where A, B, C are the rotational constants. The values of rotational constants for this molecule are (Flygare and Howe, 1962)

$A = 11518.3$ Mc/sec,

$B = 2545.1$ Mc/sec

and

$C = 2082.5$ Mc/sec.

For an asymmetric molecule

$$(2J+1)|\mu_{ij}|^2 = \mu^2_x . xS_{ij}$$

where xS_{ij} is the transition strength and μ_x is the component of the dipole moment. In this molecule the dipole moment is chiefly along the b principal inertial axis, therefore transitions involving μ_b are only important.

$F(\nu, \nu_{ij})$ is the shape factor and is given by

$$F(\nu, \nu_{ij}) = \left[\frac{\Delta\nu^2 + \nu_{ij}(\nu+\nu_{ij})}{\Delta\nu^2 + (\nu+\nu_{ij})^2} + \frac{\Delta\nu^2 - \nu_{ij}(\nu-\nu_{ij})}{\Delta\nu^2 + (\nu-\nu_{ij})^2}\right] \quad .. \quad (4)$$

It is found that in expression (2) the contribution of the term $2\Sigma_{v}\Sigma_{T} f_v f_{J_T} |\mu_{ij}|^2 \chi \left(\frac{\nu}{\nu_{ij}}\right)^2$ in comparison to μ^2 is negligible and when the third term was evaluated for some of the lines whose frequencies are near to the frequency of measurement, it was further noted that the contribution of the third term is also negligible. Thus in the present case expression (2) reduces to

$$\delta = \frac{3p(P_E+P_A)}{RT} + \frac{4\pi N}{3kT}\mu^2 \tag{5}$$

The value of dipole moment μ for this molecule is 1.9 debye. The value of the second term in Eq. (5) has been evaluated for a pressure of 21 cm Hg, N, which is the number of molecules per c.c., is given by

$$N = 9.68\times10^{18}(p/T),$$

where p is in mm and T is in degrees Kelvin, therefore $N = 9.68\times10^{18}\times210/307 = 6.521\times10^{18}$. Substituting this value of N and other constants in the second term of relation (5) it is found that

$$\frac{4\pi N}{3kT}\mu^2 = 2.36\times10^{-3}$$

Since the observed value of susceptibility at a pressure of 21 cm Hg, as shown in figure 1, is also 2.36×10^{-3}, the contribution of the first term in relation (5) is

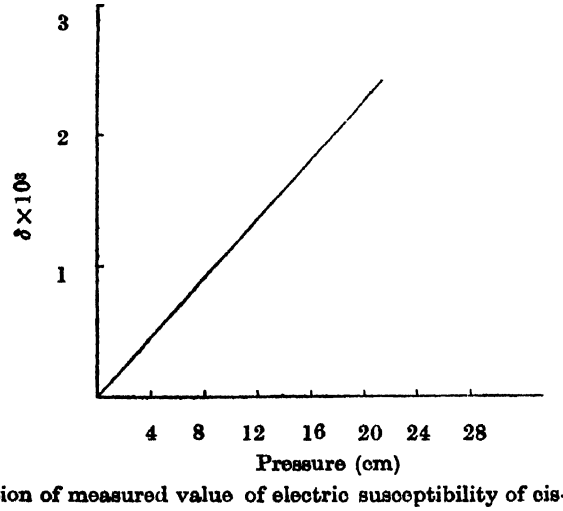

Figure 1. Variation of measured value of electric susceptibility of cis-1, 2 dichloroethylene with pressure.

negligible. The experimental accuracy in the measurement of δ is of the order of 5×10^{-5}; therefore it is obvious that the contribution of atomic and electronic polarisations is less than this value.

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